

THE EFFECT OF MOLECULAR WEIGHT ON THE COMPOSITE PROPERTIES OF CURED PHENYLETHYNYL TERMINATED IMIDE OLIGOMERS

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ABSTRACT

As part of a program to develop high temperature/high performance structural resins for aeronautical applications, imide oligomers containing terminal phenylethynyl groups with calculated number average molecular weights of 1250, 2500 and 5000 g/mol were prepared, characterized, and evaluated as adhesives and composite matrix resins. The goal of this work was to develop resin systems that are processable using conventional processing equipment into void free composites that exhibit high mechanical properties with long term high temperature durability, and are not affected by exposure to common aircraft fluids. The imide oligomers containing terminal phenylethynyl groups were fabricated into titanium adhesive specimens and IM-7 carbon fiber laminates under 0.1 - 1.4 MPa for 1 hr at 350-371°C. The lower molecular weight oligomers exhibited higher cured T_g, better processability, and better retention of mechanical properties at elevated temperature without significantly sacrificing toughness or damage tolerance than the higher molecular weight oligomer. The neat resin, adhesive and composite properties of the cured polymers will be presented.

KEY WORDS: High Temperature Polymers, Polyimides, Phenylethynyl Containing Imides, Adhesives, Carbon Fiber Composites, Oligomeric Thermosetting Imides

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1. INTRODUCTION

Structural resins with an attractive combination of properties for high temperature/high performance applications are needed for advanced aircraft, in particular high speed vehicles. These advanced materials must be readily processable under pressures and temperatures compatible with conventional manufacturing equipment currently in use or under development. Minimum mechanical performance is required as dictated by the service environment that the advanced aircraft is likely to experience during its operational lifetime such as high temperature, high stress, object impact, thermal cycling, and exposure to moisture and aircraft fluids such as hydraulic fluid, deicing fluid, paint stripping solvents, alkaline cleaning solutions, and aircraft fuels.

Over the last 6 years, work in the area of phenylethynyl containing imide oligomers have yielded some promising results (1-25). Due to their oligomeric nature, these materials exhibit excellent processability during fabrication of neat resin moldings, bonded panels, and composites under pressures of 1.4 MPa or less. Upon thermal cure for ~1 h at 350-371°C, the phenylethynyl group undergoes a complex reaction involving chain extension, branching and crosslinking without the evolution of volatile by-products to afford a pseudo three-dimensional network. The reaction products are dependent on the relative concentration, location, configuration and molecular mobility of the phenylethynyl groups and the oligomer backbone. Upon curing, the glass transition temperature (T_g) of the material increases significantly relative to that of the uncured oligomer. Although the chemistry of the cured product is not well understood, the cured oligomer exhibits an excellent combination of properties that includes high T_g , high toughness, high strength, moderate modulus, and good moisture and solvent resistance.

One phenylethynyl containing imide oligomer designated PETI-5 developed at the NASA Langley Research Center has undergone extensive evaluation as an adhesive (20-2) and composite matrix resin (23-5). The material is a random copolymer prepared from 3,4'-oxydianiline, 1,3-bis(3-aminophenoxy)benzene and 3,3',4,4'-biphenyltetracarboxylic dianhydride and endcapped with 4-phenylethynylphthalic anhydride at a calculated number average molecular weight ($\bar{M}_n$) of 5000 g/mol. This material has displayed good processability and excellent mechanical properties in adhesive and composite forms; however, improved resin flow is desired in the processing of complex structural parts. In order to improve the processability of 5000 g/mol PETI-5, lower molecular weight versions (calculated $\bar{M}_n$ of 1250 and 2500 g/mol) were prepared and characterized as neat resins, adhesives, and composite matrix resins. The chemistry, physical and mechanical properties of the oligomers and the corresponding cured polymers are discussed.

2. EXPERIMENTAL

2.1 Starting Materials The following chemicals were obtained from the indicated sources and used without further purification: 3,4'-oxydianiline (3,4'-ODA, Mitsui Petrochemical Ind., Ltd., m.p. 84°C), 1,3-bis(3-aminophenoxy)benzene (APB, Mitsui Toatsu, m.p. 107-109°C), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA, m.p. 227°C, Allco Chemical Co.), 4-phenylethynylphthalic anhydride (PEPA, Daychem Laboratories, Inc., m.p. 152°C) and N-methyl-2-pyrrolidinone (NMP, Fluka Chemical Co.).

2.1.1 Synthesis of Phenylethynyl Terminated Imide (PETI) Oligomers

Phenylethynyl terminated imide (PETI) oligomers with a calculated $\overline{M}_n$ of 1250, 2500 and 5000 g/mole were prepared by reacting BPDA with 3,4'-ODA and APB and endcapping with PEPA. Initially, the PETI oligomers were prepared as the amide acid by first dissolving the appropriate quantities of diamines (3,4'-ODA and APB) in NMP at room temperature under nitrogen. The diamine solution was subsequently cooled via an ice water bath and the dianhydride (BPDA) and endcapper (PEPA) were added in one portion as a slurry in NMP. The solids concentration was subsequently adjusted to ~35% (w/w) with additional NMP. The reactions were allowed to stir for ~24 hrs at ambient temperature under nitrogen and an aliquot was subsequently removed to determine inherent viscosity and for gel permeation chromatographic analysis to assess molecular weight and molecular weight distribution. This solution was subsequently used to prepare thin films, adhesive tape or IM-7 prepreg. Imide oligomer was prepared from the amide acid solution by subsequently fitting the flask with a Dean Stark trap and condenser, adding toluene, and refluxing the solution overnight. The imide oligomers precipitated from solution during the imidization process. The powders were isolated by adding the reaction mixture to water, washing in warm water and methanol. The yellow powders were dried to constant weight with yields >95%.

2.1.2 Films NMP solutions (30-35% w/w solids) of the phenylethynyl terminated amide acid oligomers were centrifuged, the decantate doctored onto clean, dry plate glass and dried to a tack-free form in a low humidity chamber. The films on glass were imidized and cured by heating at 100, 225 and 350°C for 1 hr each in flowing air. Thin film tensile properties were determined according to ASTM D882 using four specimens per test condition.

2.1.3 Molded Specimens Powdered imide oligomer of the 2500 g/mol PETI-5 was compression molded in a 3.2 cm² stainless steel mold under 0.3 MPa by heating to 350 or 371°C for 1 hr. Miniature compact tension specimens (1.6 cm x 1.6 cm x 0.95 cm thick) were machined from the moldings and subsequently tested to determine fracture toughness (K_{IC} , critical stress intensity factor) according to ASTM E399 using four specimens per test condition. G_{IC} , (critical strain energy release rate) was calculated using the mathematical relationship $G_{IC} = (K_{IC})^2/E$, where E is the modulus of the material.

2.1.4 Adhesive Specimens Adhesive supported film was prepared by multiple coating of 112-E glass with an A-1100 finish with a NMP solution of the amide acid oligomer (20% solids) and stage dried in a forced air oven to 225°C after each coat. After sufficient thickness had been achieved, the film was dried to 250°C for 0.5 hr. The final volatile content of the tapes ranged from ~2-4%. Standard lap shear adhesive specimens (bond area 2.54 cm wide x 1.27 cm overlap) using titanium (Ti, 6Al-4V) adherends with a PASA Jell 107 (Products Research and Chemical Corp., Semco Div.) surface treatment were fabricated in a press at 350°C under various pressures for 1 hr. Tensile shear adhesive strengths were determined according to ASTM D1002 using four specimens per test condition.

2.1.5 Composite Specimens 35% solids solutions of the amide acid oligomers in NMP ($\overline{M}_n = 1250$ and 2500 g/mole, inherent viscosity of 0.15-0.20 dL/g) with Brookfield viscosities of 2689 and 12,800 cps, respectively, at 25°C were used to coat unsized IM-7 carbon/graphite fiber (12k tow) on a multi-purpose prepregging machine. The unidirectional tapes (21.6 cm wide) exhibited resin contents ranging from 30-36% and volatile contents of ~15-19% and fiber aerial weights of ~145g/m². Laminates were fabricated in a vacuum press under 76.2 cm mercury during the entire process cycle. The laminates were fabricated by heating to 250°C over ~1 hr period and holding at 250°C for 1 hr. Pressure (0.3-0.7 MPa) was subsequently applied and the temperature ramped up over a 0.5 hr period to 371°C and held for 1 hr. The laminates were cooled under pressure to about 100°C and the pressure subsequently released. The composite panels were ultrasonically scanned (C-scanned), cut into specimens and tested for mechanical properties according to ASTM procedures.

2.1.6 Other Characterization Inherent viscosities (η_{inh}) were obtained on 0.5% (w/v) solutions of the amide acids in NMP at 25°C. Differential scanning calorimetry (DSC) was conducted on a Shimadzu DSC-50 thermal analyzer at a heating rate of 20°C/min with the T_g taken at the inflection point of the ΔT versus temperature curve. Dynamic thermogravimetric analyses (TGA) were performed on a Seiko 200/220 instrument on cured polymer powder samples at a heating rate of 2.5°C/min in air at a flow rate of 15 cm³/min. Brookfield viscosity was obtained on a Brookfield LVT Synchro-Lectric viscometer at 25°C. Rheological measurements were conducted on a Rheometrics System 4 rheometer. Sample specimen disks, 2.54 cm in diameter and 1.5 mm thick, were prepared by press molding imide powder at room temperature. The compacted resin disk was subsequently loaded in the rheometer fixture with 2.54 cm diameter parallel plates. The top plate was oscillated at a fixed strain of 5% and a fixed angular frequency of 10 rad/sec while the lower plate was attached to a transducer which recorded the resultant torque. Storage (G') and loss (G'') moduli as a function of time (t) were measured at several temperatures. Gel permeation chromatography (GPC) was performed on a Waters 150C system equipped with a model 150R differential viscosity detector and a differential refractive index detector. GPC analyses were performed on dilute solutions of the amide acids in freshly distilled NMP containing 0.02M phosphorus pentoxide. The analyses were performed using a two column bank consisting of a linear

Waters Styragel HT 6E column covering the molecular weight range of 10^3 to 10^7 g/mole in series with a Styragel HT 3 column covering the molecular weight range of 10^2 to 10^4 g/mole. A universal calibration curve was generated with Polymer Laboratories narrow molecular weight distribution polystyrene standards having molecular weights ranging from 500 to 2.75×10^6 g/mole.

3. RESULTS AND DISCUSSION

3.1 Synthesis of Amide Acid and Imide Oligomers of PETI-5 of Different Number Average Molecular Weights An oligomer designated PETI-5, which was developed at NASA Langley Research Center, was prepared from 3,4'-ODA, APB and BPDA at a calculated $\bar{M}_n$ of 5000 g/mol and endcapped with PEPA. Good processability was evident in the fabrication of moldings, adhesives and laminates; however, during the fabrication of complex composite structures, small areas of the part with tight bends exhibited some porosity, indicating the need for a resin with more flow. In order to improve the processability of PETI-5 (calculated $\bar{M}_n$ of 5000 g/mol), lower $\bar{M}_n$ versions (calculated $\bar{M}_n$ of 1250 and 2500 g/mol) were investigated.

The PETI-5 oligomers were prepared through the amide acid route in NMP with subsequent cyclization to the corresponding imide oligomer (Fig. 1). Initially, the diamines were dissolved in NMP and the solution cooled to $\sim 15^\circ\text{C}$. BPDA and PEPA were then added in one portion as a slurry in NMP to the stirred solution and the solids content adjusted to $\sim 35\%$ with NMP. The stirred solution was then allowed to warm to ambient temperature under nitrogen. From these solutions thin films, supported adhesive film, and unidirectional IM7 carbon fiber tape were prepared. An aliquot from each of these solutions was removed to assess the molecular weight and distribution. Imide powders were prepared by cyclodehydration of the precursor amide acid oligomers by azeotropic distillation in the presence of toluene for ~ 24 hrs. As the imide oligomers formed, they precipitated from solution.

Oligomer characterization is presented in Table 1. For comparative purposes the data for 5000 g/mol PETI-5 is included. The initial Tgs of the oligomers were $170\text{--}210^\circ\text{C}$ with melting transitions (Tms) ranging from $320\text{--}357^\circ\text{C}$. After melting, the samples failed to recrystallize upon annealing. After a thermal cure for 1 hr at 371°C , no Tms were evident. Powdered samples that were cured in a sealed DSC pan at 371°C for 1h, exhibited increases in Tg of $\sim 60\text{--}118^\circ\text{C}$ and followed the trend $1250\text{ g/mol} > 2500\text{ g/mol} > 5000\text{ g/mol}$. This was as expected since the 1250 and 2500 g/mol versions contained 64 and 34 mole % PEPA, respectively, as compared to the 5000 g/mol version which contained 18 mole % PEPA. As observed for other PETIs, the exothermic onset and peak due to the cure reaction of the phenylethynyl groups occurred at $\sim 390^\circ\text{C}$ and $\sim 450^\circ\text{C}$, respectively. The temperature of 5% weight loss as measured by dynamic TGA in air on imide powder cured for 1 hr at 371°C ranged from $489\text{--}503^\circ\text{C}$ and was comparable to that of other phenylethynyl containing imide oligomers.

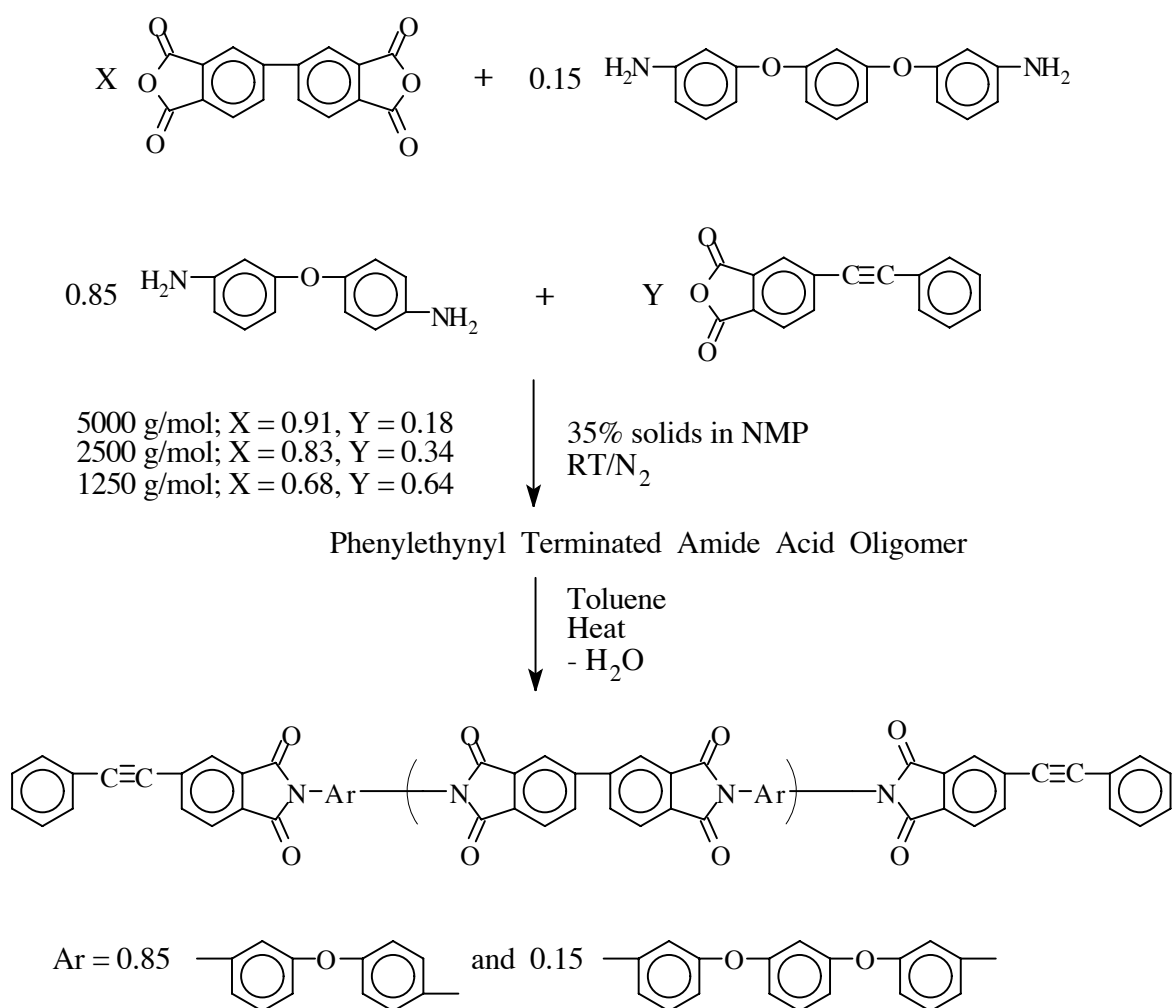


Figure 1. Preparation of PETI-5 oligomers at calculated $\overline{M}_n$ of 1250, 2500, and 5000 g/mol.

Table 1. Physical Properties

Calculated $\overline{M}_n$ (g/mole)	η_{inh} , dL/g ¹	T_g (T_m), °C ²		TGA, 5% Wt. Loss, °C ⁴
		Initial	Cured ³	
1250	0.15	170 (320)	288	489
2500	0.20	210 (330)	277	497
5000	0.27	210 (357)	270	503

1. Determined on 0.5% (w/v) NMP solutions of the amide acid at 25°C.

2. Determined on powdered samples by DSC at a heating rate of 20°C/min.

3. Determined on powdered samples cured in a sealed DSC pan for 1 h at 371°C.

4. Determined on powdered samples in air at a heating rate of 2.5°C/min.

GPC analyses were performed on as-prepared amide acid solutions of the different $\overline{M}_n$ versions of PETI-5 to assess molecular weight and molecular weight distribution with the data presented in Table 2. In general, the $\overline{M}_n$ determined by GPC were greater than the calculated $\overline{M}_n$. Several shoulder peaks at the low molecular weight end of the molecular weight distribution curve were obtained for the 1250 g/mol PETI-5. A more Gaussian type of

distribution was observed for the 2500 g/mol PETI-5 with a slight shoulder evident at the low molecular weight end.

Table 2. GPC Analysis of PETAA-5 Oligomers

Calculated $\overline{M}_n$ (g/mole)	$\overline{M}_n$, g/mole	$\overline{M}_w$, g/mole	$\overline{M}_z$, g/mole	Polydispersity
1250	2050	3022	4307	1.47
2500	3308	6022	11670	1.82
5000	7914	13865	24260	1.75

3.1.1 Films Unoriented thin films were cast from NMP solutions of the amide acid oligomers and cured in flowing air to 350°C. Thin film tensile properties are presented in Table 3. Tensile strength and modulus at room temperature of the 2500 g/mol PETI-5 were ~15% greater than those obtained for the 5000 g/mol version. When tested at 177°C, the strengths and moduli for both $\overline{M}_n$ versions were comparable. The elongation to break of both $\overline{M}_n$ versions was high and indicative of a linear thermoplastic material rather than a thermoset suggesting that the thermal cure reaction of the phenylethynyl group leads to the formation of a high degree of chain extension. A film of the 1250 g/mol PETI-5 had variable thickness due to excessive resin flow during the oven cure; however, the film was flexible and creasable indicating reasonable toughness.

Table 3. Unoriented Thin Film Tensile Properties

Calculated $\overline{M}_n$ (g/mole)	Test Temp., °C	Str., MPa	Mod., GPa	Elong. @ Break, %
2500	23	151.7	3.5	14
	177	76.6	2.2	43
5000	23	129.6	3.1	32
	177	84.1	2.3	83

3.1.2 Neat Resin Moldings Fracture toughness was determined on cured moldings of the 2500 g/mol version of PETI-5 at room temperature. The moldings were prepared from solution imidized powder in a stainless steel mold under 0.3 MPa by heating to 350 or 371°C for 1 hr. The moldings were well consolidated and exhibited a small amount of flash. The fracture toughness (K_{IC} , critical stress intensity factor) values for the 2500 g/mol and 5000 g/mol PETI-5 cured at 350°C for 1 h were identical (Table 4). This was unexpected since typically lowering the molecular weight results in a more brittle material due to the increased crosslink density. The G_{IC} s were different due to the difference in the tensile moduli of the two materials. The higher cure temperature (371°C) for the 2500 g/mol PETI-5 resulted in a minimal decrease in the K_{IC} . Flash from both of the 2500 g/mol PETI-5 moldings exhibited Tgs of 279°C and no melting transitions.

Fabrication conditions were not developed to obtain good quality compact tension specimens of the 1250 g/mol PETI-5. This oligomer exhibited high resin flow. A 2.54 cm x 0.32 cm disk of the 1250 g/mol PETI-5 was tough and was fabricated by B-staging the powder to 300°C for 0.17 hr with a subsequent cure for 0.5 hr at 345°C. When these conditions were used to fabricate a compact tension specimen, the molding had voids presumably due to air. The high toughness exhibited by both $\overline{M}_n$ versions is characteristic of a thermoplastic material and further supports that the cure of the terminal phenylethynyl groups leads to a high degree of chain extension.

Table 4. Neat Resin Fracture Toughness

Calculated $\overline{M}_n$ (g/mole)	K_{IC} , MPa·m ^¼	G_{IC} , J/m ²
2500 ¹	3.9	4261
5000 ¹	3.9	4295
2500 ²	3.7	3878

1. Molding cured for 1 hr at 350°C.
2. Molding cured for 1 hr at 371°C.

3.1.3 Adhesives Supported adhesive films of 1250 and 2500 g/mol PETI-5 were prepared by multiple coating of 112 E-glass and stage-drying up to 225°C in air after each coat. After sufficient thickness had been achieved, the films were dried to 250°C for 0.5 hr. The final volatile content of the tapes were ~1% and ~4% for the 1250 and 2500 g/mol PETI-5, respectively. The high volatile content of the 2500 g/mol PETI-5 was planned in

Table 5. Preliminary Adhesive Properties

Calculated $\overline{M}_n$ (g/mole)	Bonding Conditions	Test Temp., °C	Tensile Shear Str., MPa
1250	0.03 MPa @ 350°C for 1 hr	23	21.3
		177	27.0
		200	25.9
2500	0.1 MPa @ 350°C for 1 hr	23	36.6
		177	28.6
		200	27.0
5000	0.7 MPa @ 350°C for 1 hr	23	49.0
		177	29.7

order to minimize cracking and flaking of the tape due to the $\overline{M}_n$ of the oligomer. The tape was of excellent quality and did not exhibit any cracking or flaking. A good quality tape of the 1250 g/mol PETI-5 was obtained, but it flaked upon cutting. Specimens were fabricated using titanium adherends with a PASA Jell 107 surface treatment and primed with the amide acid of the 5000 g/mol PETI-5 by heating to 350°C for 1 hr. The tensile shear strengths are presented in Table 5. For comparative purposes, tensile shear properties of 5000 g/mol PETI-5 are included.

The 2500 g/mol PETI-5 specimens exhibited lower tensile shear strengths at room temperature than the 5000 g/mol version. Comparable strengths were obtained at 177°C for both $\overline{M}_n$ versions. The failures were cohesive for both systems at both test conditions.

The 1250 g/mol PETI-5 exhibited lower tensile shear strengths at room temperature than the 2500 and 5000 g/mol PETI-5. The tensile shear strengths at 177°C were comparable to the other $\overline{M}_n$ versions. The failure mode was predominantly adhesive with increasing mixed failures at elevated temperature.

3.1.4 Rheology Dynamic rheological properties, G' (t) and G'' (t), were measured on powder molded discs of the 1250 and 2500 g/mol PETI-5. The test chamber of the rheometer was at room temperature prior to loading the specimen and a temperature profile simulating a composite fabrication cycle was followed. The specimen was heated from 23 to 250°C at a heating rate of 4°C/min and held for 1 hr. The sample was subsequently heated to 371°C at the same heating rate and held for 0.5 hr. The results are shown in Table 6. As expected decreasing the $\overline{M}_n$ lowered the minimum melt viscosity. All of these materials exhibited their respective minimum melt viscosities at temperatures where the phenylethynyl groups react. Thus, the minimum melt viscosities for all of these materials are not stable at these temperatures.

Table 6. Melt Rheology

Calculated $\overline{M}_n$ (g/mole)	Minimum Melt Viscosity, Poise	Temp., °C
1250	50	335
2500	900	335
5000	10,000	371

3.1.5 Composites IM-7 carbon fiber composites of 1250 and 2500 g/mol PETI-5 were fabricated from solution coated unidirectional tape in a vacuum press under 0.3 and 0.7 MPa, respectively, with a final cure at 371°C for 1 hr. Acceptable tack of the 1250 and 2500 g/mol PETI-5 was obtained at a lower volatile content as compared to that for the 5000 g/mol PETI-5. The processing cycle for these laminates is presented in Figure 2 and was originally developed for the 5000 g/mol PETI-5. Other than a reduction of the applied pressure due to the better flow of the 1250 and 2500 g/mol versions, no optimization work was performed. The laminates generally exhibited excellent C-scans indicating good consolidation with little

or no void content. The composite properties are presented in Table 7. For comparative purposes, IM-7 composite properties of the 5000 g/mol PETI-5 are also presented.

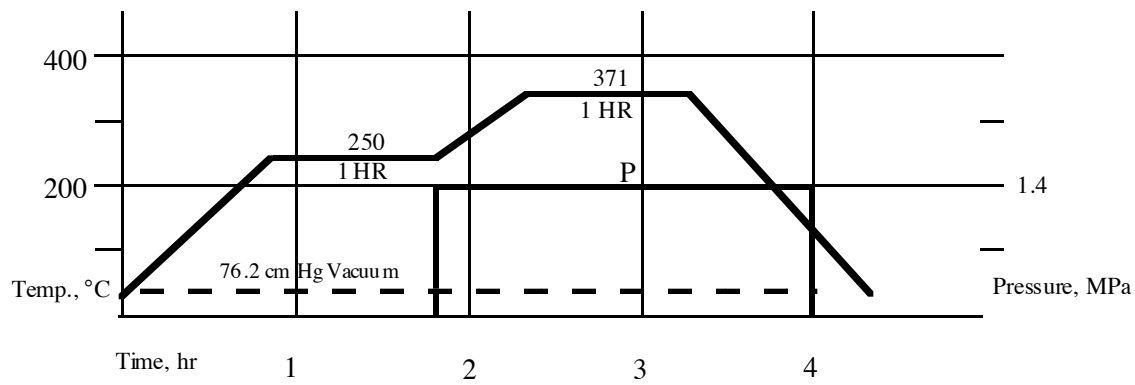


Figure 2. Laminate Processing Cycle for PETI-5 oligomers at calculated $\overline{M}_n$ of 1250, 2500, and 5000 g/mol.

The compression strengths after impact (CAI) were obtained on quasi-isotropic laminates which were impacted at a stress of 30.5 J prior to testing. The open hole compression (OHC) strengths were obtained on laminates with 58% of the plies in the zero orientation (lay-up 58/34/8). The 2500 and 5000 g/mol PETI-5 exhibited comparable OHC (RT, dry), CAI strength and modulus, and microstrain. Better retention of the OHC (177°C, dry) properties was exhibited by the 2500 g/mol PETI-5 as compared to the 5000 g/mol version. The 1250 g/mol PETI-5 exhibited comparable OHC properties to the 2500 and 5000 g/mol PETI-5,

Table 7. IM-7/PETI-5 Laminate Properties

Property	1250 g/mol	2500 g/mol ¹	5000 g/mol ¹
OHC Str., MPa			
RT (dry)	431.6	458.6	450.3
177°C (dry)	366.2	395.2	342.7
177°C (wet)	368.5	344.1	-----
CAI Str., MPa			
(25/50/25)	244.6	334.5	331.0
CAI Mod., GPa			
(25/50/25)	55.8	57.9	55.9
Microstrain, $\mu\text{in/in}$	4377	5908	5986
Thermal Cycling Microcracks/in. after 200 cycles ²	0	0	0

1. Normalized to 62% fiber volume.
2. After 200 thermal cycles from -55 to 177°C with a 1 hr hold at each temperature and a heating rate of 8.3°C/min.

however, the CAI strength and microstrain were reduced. The 1250 g/mol PETI-5 laminates had low resin contents (26-28%) due to excessive resin flow during fabrication. Consequently, the composite properties in Table 7 were not normalized. Thus it may not be prudent to compare the laminate properties of the 1250 g/mol version with the others.

Specimens of the 1250 and 2500 g/mol PETI-5 were tested for microcrack resistance. The tests were performed on crossply laminates which were thermally cycled from -55 to 177°C at a heating rate of 8.3°C/min with a 1 hr hold at each temperature. The specimens were examined after 100 and 200 cycles under a microscope for microcracks. Neither sample exhibited any microcracks.

4. SUMMARY

PETI-5 was prepared at calculated $\overline{M}_n$ s of 1250 and 2500 g/mol and characterized as unoriented thin films, neat resins, adhesives, and composite matrix resins and compared to the 5000 g/mol PETI-5. The 1250 g/mol PETI-5 exhibited excessive resin flow in film, molding, adhesive, and composite forms. Similar mechanical properties and better processability were obtained for the 2500 g/mol version as compared to the 5000 g/mol PETI-5. Thus, the 2500 g/mol PETI-5 has the potential to offer processing improvements in the fabrication of complex composite structures without sacrificing the excellent properties of the 5000 g/mol version.

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The use of trade names of manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

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7. Biographies

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